METHOD OF RECOVERY OF HYDROCARBONS FROM SOLID HYDROCARBONACEOUS FORMATIONS

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ABSTRACT OF THE DISCLOSURE

This invention relates to a method for retorting oil shale formations wherein at least three and preferably at least four wells are employed in an oil shale formation and such wells are connected by a substantially horizontal permeable material. It is preferred to employ at least three wells equally spaced from one another around the periphery of a portion of the formation and at least one well centrally located within such portion of the formation. Initially water is injected into the central well, a hydrocarbon having a temperature of at least 600°F. is injected into at least one of the peripheral wells, an unheated hydrocarbon is injected into at least one other peripheral well and product hydrocarbons are withdrawn from another of such peripheral wells. After a period of time, the flows in the peripheral wells are alternated by injecting the heated hydrocarbons into the well originally used for removal of hydrocarbon product, injecting unheated hydrocarbons into the well originally receiving heated hydrocarbons and removing product hydrocarbons from the well originally receiving unheated hydrocarbons. After a period of time the hydrocarbon flows are again alternated in the same manner.

This invention is related to a method for the recovery of hydrocarbons from solid hydrocarbonaceous materials and is more particularly directed to a method for the destructive distillation of oil shale to produce hydrocarbons therefrom. It is known that hydrocarbons may be recovered by the destructive heating of such formations as oil shale and coal deposits. The recovery of valuable hydrocarbon products from such sources, particularly certain sedimentary rocks which are commonly referred to as oil shale, has been sought for many years and numerous processes have been developed whereby relatively crude oil, as well as gaseous hydrocarbons, may be produced therefrom. Extensive deposits of oil shale are to be found in this country, particularly in the so-called Green River Shale formations located in the states of Colorado, Utah and Wyoming. Important shale deposits are also found in other parts of the world. With diminishing world petroleum reserves and accelerating world demand for petroleum products there exists a necessity for developing a commercial feasible process for recovering the hydrocarbon values from other sources.

The organic matter contained within oil shale is generally referred to as kerogen. This material generally occurs as 10 to 20 percent of the total weight of the shale, the remainder being inorganic, but this range of organic matter may be as low as 1% or less or as high as about 40%. One method for the recovery of hydrocarbons from oil shale involves mining of the shale by conventional methods and heating it in a separate step to 800°F. to 1000°F. to volatilize or destructively distill the hydrocarbon materials therefrom. Such a heating or destructive distillation step is generally referred to as "retorting" the shale. This procedure, however, involves the handling and disposal of enormous quantities of the inorganic portion of the shale and such methods have not generally proved economically feasible. Therefore, it was proposed to heat or retort the oil shale in place. Attempts have been made to accomplish this by electrically heating the formation but the electrical energy requirements have been found to be too high. Likewise, oil shale has been retorted in place by burning the organic matter with an oxygen-bearing gas. This method has proved unsatisfactory, however, as the temperatures required for maintaining the combustion also cause thermal decomposition of inorganic matter present, particularly of the mineral carbonates. Such decomposition is highly endothermic, so the total sensible heat required to retort the shale has been found to be uneconomical.

Even though extensive interest is still present in these formations, no process commercially feasible for the recovery of hydrocarbon values, e.g. mineral oil from oil shale has heretofore been available in the United States.

It is therefore an object of this invention to provide an improved process for the recovery of hydrocarbon values from oil shale and other solid hydrocarbonaceous formations. It is a further object of this invention to provide an economical process whereby such formations may be destructively distilled in place and valuable hydrocarbon products obtained therefrom. It is a further object of this invention to provide such a process which permits essentially continuous operation and is adaptable to large scale operations. These and other objects and advantages of the present process will become obvious from a reading of the following detailed specification.

It has now been discovered that hydrocarbons may be efficiently produced from naturally occurring solid hydrocarbonaceous formations by providing several, i.e. at least three and preferably four or more wells into said formation, said wells being placed in spaced relation to one another; injecting through at least one of said wells a sufficient quantity of acid to produce a horizontal permeable section within said formation which joins said wells; subsequently and alternately injecting into separate wells heated and unheated hydrocarbons to retort said formation; withdrawing from at least one such well the hydrocarbons thus produced; and injecting water into the formation through at least one of said wells previously used for injection of acid.

While the process described herein is particularly directed to oil shale, it may likewise be employed on other solid hydrocarbonaceous formations or deposits such as coal or lignite.

For the efficient continuous production of hydrocarbons from such a formation it is necessary to drill a minimum of four holes or wells from the surface of the ground to a point near the bottom of the shale or other formations to be retorted. One of such holes should be centrally located with the other holes or wells being circumferentially located around the portion of the formation to be retorted. The casing to the peripheral holes will then usually be sealed to the formation at a short distance below the upper portion of the oil shale formation to prevent leakage from the shale to the formation above. The number of holes for any given formation will depend somewhat upon the size and nature of the formation to be treated. However, less than four holes will generally not permit continuous operation but any number greater than four wells can be operated efficiently. With larger formations and the employment of a larger number of peripheral wells, more than one central well may be employed.

For relatively shallow formations, e.g. formations less than about 50 ft. thick, and for the initial retorting
stages even in large formations, it is possible and sometimes desirable to employ only three wells. These wells must be connected by a substantially horizontal permeable section within the formation and are preferably spaced more less equidistant from one another. In this arrangement, using three wells, A, B, and C, respectively, the order in which fluids are fed to and withdrawn from the different wells is alternated in successive stages. The following are a series of preferred successive stages involving in the respective stages the indicated steps of feeding fluids to and withdrawing them from the respective wells:

**Fluid flow to or from well**

<table>
<thead>
<tr>
<th>Stage</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Heated hydrocarbons fed to the well</td>
<td>Water fed to the well</td>
<td>Water and hydrocarbons withdrawn from the well</td>
</tr>
<tr>
<td>2</td>
<td>Water fed to well</td>
<td>Water and hydrocarbons withdrawn from well</td>
<td>Heated hydrocarbons fed to well</td>
</tr>
<tr>
<td>3</td>
<td>Water and hydrocarbons withdrawn from well</td>
<td>Water fed to the well</td>
<td>Water fed to well</td>
</tr>
</tbody>
</table>

The flows are alternated in this manner every 60 to 240 hours, preferably every 120 to 240 hours, until the formation is completely retorted or until the system becomes inefficient. If the system becomes inefficient, at least one more well is provided and the preferred process may be employed, as described herein, which requires at least four wells. The following is a description of the process as applied using four or more wells in the shale formation.

As hereinbefore indicated, before retorting of the formation begins, a permeable section must be established between the wells and generally along a natural horizontal parting plane such as occurs in most sedimentary deposits, e.g. in the Colorado oil shales. This permeable section is preferably established along a parting plane near the bottom of the formation. Such a permeable section is produced by known techniques such as introducing an aqueous solution, such as hydrochloric acid, through the central well at a pressure sufficient to cause a flow to the peripheral wells along the parting plane selected. This treatment will leach the mineral carbonate content of the oil shale adjacent to the parting plane, leaving a highly permeable path between the central well and the peripheral wells. The pressure required to cause the acid to flow along the parting plane will generally be dependent upon the thickness of the overburden above the parting plane. Such procedures for forming highly permeable areas within underground formations are well known and widely practiced.

Once a permeable section or zone has been established which connects the wells, a stream of hydrocarbons heated to a temperature of at least 600°F and preferably at least 750°F is injected into one of the peripheral wells. At the same time a stream of heated hydrocarbons is injected into another of the peripheral wells and product is withdrawn from the third peripheral well. As the solid hydrocarbonaceous formation is retorted, water or other material which is non-reactive with and immiscible in hydrocarbons is fed into the central well to fill the porous structure left by the retorted hydrocarbons and thereby prevent this porous structure from reabsorbing hydrocarbons. After a period of time sufficient to substantially heat the formation around the well having fed therein the heated hydrocarbon, all of the flows except the water are shifted. The heated hydrocarbon is now passed through the well from which product had been removed, unheated hydrocarbons are injected into the well where heated hydrocarbons had been passed previously and product is removed from the well wherein unheated hydrocarbons had been injected. After a period of time sufficient to substantially heat the formation around the well having heated hydrocarbons injected therein, the flows are again switched in the same manner and this process is continually repeated until such formation is substantially depleted. It is generally preferred to alternate the heated, unheated and product hydrocarbon flows every 60 to 240 hours with some advantage being gained by alternating the flows every 120-240 hours. Such period may be shorter or longer, however, depending on the type and size of the formation to be treated, the number of wells employed and the other conditions of operation.

The heated hydrocarbons to be injected in the well at a temperature of greater than 600°F should be thermally stable at the temperature employed and should generally be a hydrocarbon fraction containing 50% by weight or more of C4 to C12 hydrocarbons. Such hydrocarbons may be saturated or unsaturated aliphatic or aromatic hydrocarbons, but usually a mixture is employed. It is preferred to inject such hydrocarbons into the formation at a temperature of 750°F or greater but generally temperatures of above 1100°F are not required for effective retorting.

The unheated hydrocarbon stream to be injected into the formation is preferably at or near room temperature and is preferably not at a temperature substantially in excess of 300-400°F. The unheated hydrocarbons for such injection should generally have a viscosity of less than 2 centipoise at 100°F. Since the unheated hydrocarbons to be injected into the formation will generally be a portion of the product stream from the formation, such hydrocarbons may be at an elevated temperature. Such hydrocarbons from the product stream, although at a temperature usually considerably higher than room temperature, are included in the term "unheated hydrocarbons" as no additional heat need be added before re-injection into the formation. If the product stream should be at a temperature greater than 400°F, cooling, preferably to 300°F or lower, would be necessary prior to re-injection.

By intermittently injecting heated and unheated hydrocarbons into the peripheral wells, the regenerative principal can be used to carry heat far into the formation. If only hot hydrocarbons were injected, only the shale immediately adjacent to the peripheral wells would be heated to retorting temperature and the continuity of the path of unretorted shale between the wells to which the fluid is circulated could not be maintained. In this process, the operating pressure is determined primarily by the requirement that the pressure must be adequate to prevent gross vaporization of any aqueous phase in the retorted section. This operating requirement can be minimized by adding to the formation a concentrated solution of sodium chloride or calcium chloride in water. When water alone is contained in the formation, the pressure should be in the range of 1000 p.s.i.g. to 3000 p.s.i.g. for preferred operation. For most situations the fluid head on the inlet of the holes or wells will be adequate. For formations where little or no water is present, it is advantageous to inject water through the central well or wells and such aqueous phase is maintained in the bulk of the volume of the retorted shale. The aqueous phase, therefore, prevents the absorption of oil into the retorted shale. Since retorted shale contains about 30 percent by volume of voids, the use of water in this manner is necessary for a high recovery of oil. This use of water flooding is not usually necessary until a substantial area of the formation has been retorted.

After the formation of a permeable plane connecting the wells and after retorting of the formation has begun, it is necessary for efficient operation to add water or some other material to the formation to fill the porous material which remains after the hydrocarbon has been retorted therefrom. While water is usually available and therefore generally is preferred for this purpose, waste waters, brines, waste liquors or other low viscosity fluids not re-
active nor miscible with the hydrocarbons may be employed. Likewise, additives, such as surfactants, may be added to the water or other liquid material to enhance its ability to enter the pores of the structure.

FIGURE 1 is a schematic illustration of the proposed process.

FIGURE 2 is a plan view showing a suitable spaced relation of the wells to one another.

FIGURE 3 is a plan view showing a suitable spaced relation between the wells when only three wells are employed.

Referring to FIGURE 1, an acid, such as hydrochloric acid, is introduced into well 10 through line 11 under sufficient pressure to produce a permeable section connecting all of the wells along a parting plane. Once a permeable section has been thus established, a C₃ and C₁₀ petroleum hydrocarbon fraction, at a temperature of 750°F, is pumped into the formation from line 12 through line 27 and into well 13 by opening or closing the proper valves 28.

At the same time, unheated hydrocarbons are fed through line 14 into line 29 and into well 15 by operation, in evident manner, of the proper valves 28. Hydrocarbons retorted and extracted from the formation together with hydrocarbons fed into the formation and some water are continuously withdrawn through well 16 and passed through line 18 by operation of the proper valves 28 to line 17 and pass to a gas-liquid separator 18.

From the gas-liquid separator 18, the gaseous hydrocarbons pass overhead through line 22 as a gaseous product and the liquid portion passes through line 20 to an H₂O-hydrocarbon separator 21. The aqueous phase is removed through line 19 and preferably is returned to the formation together with such make-up water as may be required to fill a major portion of the retorted formation by passing through line 11 into well 10, the central well. The hydrocarbons are removed from the separator 21 through line 23 and passed to a hydrocarbon separator 24 which divides the liquid hydrocarbons into various viscosity fractions. A portion of the hydrocarbons containing the C₃ to C₁₀ fraction are passed through line 25 to heater 26 where they are heated to 750°F, and returned to the formation through line 12, line 27 and well 15. Another portion of the hydrocarbons are returned to the formation through line 14 into well 15. This hydrocarbon fraction has a viscosity less than 2 centipoise at 100°F, and is returned unheated through line 14 and line 29 to well 15. The remaining liquid hydrocarbons are removed from the system as product for further separation, treatment or sale. Hydrocarbon separator 24 is originally filled with hydrocarbons to begin the retorting operation.

After operating continuously for 120 hours in this manner, the flows are halted and switched by proper operation of the valves 28. The heated hydrocarbons from line 12 are passed through line 30 and into well 16, the unheated hydrocarbons from line 14 are passed through line 27 and into well 13 and product is removed from well 15 through line 29 to line 17. The hydrocarbons and water are separated as before and portions thereof returned to the formation.

After operating in this manner continuously for 120 hours, the flows are again halted and switched by proper operation of the valves 28. The heated hydrocarbons from line 12 are passed through line 29 and into well 15, the unheated hydrocarbons from line 14 are passed through line 27 and into well 16 and product is removed from well 13 through line 27 to line 17. The hydrocarbons and water are separated as before and portions thereof returned to the formation.

After operating in this manner continuously for 120 hours, flows to and from the three peripheral wells are again switched to their original position. During the entire process, water is fed into line 11 and well 10 at a rate substantially equivalent to the rate of removal of hydrocarbons from the formation.

Hydrocarbons are produced from the formation at a rate equal to about 10% by weight of the hydrocarbons fed into the formation. The hydrocarbons thus produced generally have a gravity of about 20° API and a viscosity of about 50 centipoises at 100°F.

FIGURE 2 shows the spaced relationship of peripheral wells 13, 15 and 16 to one another and to central well 10. Additional peripheral wells would preferably be spaced as equidistant as possible from the other wells. The description of FIGURE 1 where the flows are periodically rotated shows a rotation counterclockwise around the arrangement of FIGURE 2.

FIGURE 3 shows a preferred arrangement of the wells where only three wells are employed. Such arrangement may be modified, however, to fit the requirements of a particular situation or to conform to the configuration of a particular formation. In the case of a shallow formation or the beginning of operations on a large formation, a configuration such as shown in this FIGURE 3 may be employed. Once a permeable section is established in the formation which interconnects the wells, a C₃ to C₁₀ petroleum hydrocarbon fraction, at a temperature of 750°F, is pumped into the formation through well 31 and water which is liquid at the well pressure is simultaneously pumped into well 32. A mixture of the hydrocarbons fed into the formation, hydrocarbons retorted from the formation and water are then recovered from well 33.

The products thus obtained are separated and are as described fully in the discussion of FIGURE 1, with the water and a portion of the hydrocarbon effluent being returned to the formation.

After operating continuously for 120 hours in this manner, the flows are stopped and switched such that the heated hydrocarbon is fed into well 33, liquid water is fed into well 31 and product hydrocarbon and water are withdrawn from well 32 and separated as before.

After operating in this manner for an additional 120 hours, the flows are stopped and switched such that heated hydrocarbon is fed into well 33, liquid water is fed into well 31 and product hydrocarbons and water are withdrawn from well 31 and separated as before.

This procedure is continued until the formation is substantially completely retorted or until this procedure becomes inefficient, at which time one or more additional wells may be drilled and the process is continued using the well arrangement of FIGURE 1 of the drawings.

I claim:

1. A method for the production of hydrocarbons from naturally occurring solid hydrocarbonaceous formations which comprises providing at least four wells into said formation wherein at least three of said wells are spaced from one another around the periphery of a portion of such formation and at least one such well is located centrally within said portion of such formation, providing a substantially horizontal permeable section within said formation which joins all of said wells, injecting water continuously into said central well, injecting into at least one of said peripheral wells a hydrocarbon at a temperature greater than 600°F, injecting into at least one other of said wells an unheated hydrocarbon, withdrawing from at least one other of such wells the hydrocarbons thus produced and injecting into at least one central well a low viscosity oil-immiscible fluid, subsequently retorting said flows by injecting said heated hydrocarbon into the wells originally used for removal of the hydrocarbon product, injecting unheated hydrocarbons into the wells originally receiving heated hydrocarbons and removing product hydrocarbons from those wells originally receiving unheated hydrocarbons.

2. The process of claim 1 wherein said flows are alternated every 60 to 120 hours.

3. The process of claim 1 wherein the permeable section is provided by injecting an aqueous solution of an acid into at least one centrally located well prior to retorting of the formation.

4. A method for the production of hydrocarbons from
naturally occurring solid hydrocarbonaceous formations which comprise providing at least four wells into said formation wherein at least three of said wells are equally spaced from one another around the periphery of a portion of such formation and at least one such well is located centrally within said portion of such formation, providing a substantially horizontal permeable section within said formation which interconnects such wells, injecting water into said central well, injecting into at least one of said peripheral wells a hydrocarbon at a temperature of at least 750° F., injecting into at least one other of said wells an unheated hydrocarbon, withdrawing from at least one other of such wells the hydrocarbons thus produced and injected into at least one central well a low viscosity oil-immiscible fluid, subsequently alternating said flows by injecting said heated hydrocarbon into the wells originally used for removal of the hydrocarbon product, injecting an unheated hydrocarbon into the wells originally receiving heated hydrocarbons and removing product hydrocarbons from those wells originally receiving unheated hydrocarbons, again alternating said flows by injecting a heated hydrocarbon into the wells originally receiving an unheated hydrocarbon, injecting an unheated hydrocarbon into the wells originally used for removal of the product hydrocarbons and removing product hydrocarbons from the wells originally receiving a heated hydrocarbon.

5. The process of claim 4 wherein said flows are alternated every 60 to 120 hours.

6. The process of claim 4 herein said flows are alternated every 60 to 120 hours until such portion of said formation is substantially completely retorted.

7. The process of claim 4 wherein the permeable section is provided by injecting an aqueous solution of an acid into at least one centrally located well prior to retorting of the formation.

8. The process of claim 4 wherein the low viscosity oil-immiscible fluid is water.

9. A method for the production of hydrocarbons from naturally occurring solid hydrocarbonaceous formations which comprises providing at least three wells into said formation wherein said wells are substantially equidistant from one another, providing a substantially horizontal permeable section within said formation which joins all of said wells, injecting into at least one such well a hydrocarbon at a temperature greater than 600° F., injecting liquid water into at least one other such well, withdrawing from at least one other such well the hydrocarbons thus produced together with portions of the hydrocarbons and water fed into such formation; subsequently alternating said flows by injecting said heated hydrocarbon into said well originally used for recovery of hydrocarbon product, injecting liquid water into said well originally used for heated hydrocarbons and recovering product hydrocarbons from the well originally used for the injection of heated water; subsequently injecting said heated hydrocarbons into the well originally used for the injection of liquid water, injecting liquid water into the well originally used to remove hydrocarbon product and withdrawing hydrocarbon product from the well originally receiving heated hydrocarbon.

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